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Structural Consequences of the Prohibition of Hydrogen Bonding in Copper–Guanidine Systems

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The synthesis and structure of copper(I) complexes supported by N-substituted bicyclic guanidines is described. The *N*-methyl-substituted bicyclic guanidine 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine (hppMe) reacted with copper(I) chloride to afford the ion-pair $[Cu(hppMe)_2][CuCl_2]$ (**1**), a rare example of a compound containing an unsupported Cu···Cu interaction. The analogous reaction with CuI, however, afforded the molecular μ,μ-dihalo-bridged dimer $[CuI(hppMe)]_2$ (**2**). Inclusion of a trimethylsilyl substituent at nitrogen provided a sufficiently sterically encumbered environment to support a two coordinate copper center in $CuCl(hppSiMe_3)$ (**3**). Compounds **1**–**3** have been fully characterized, including single-crystal X-ray diffraction studies.

Introduction

Copper is the key element in a number of biological transformations involving small molecules mediated by metalloenzymes.[1] Molecular systems which mimic the interactions of the protein with the copper atom are important in understanding such processes, and on a fundamental level, the way in which ligands containing component functionalities from proteins bind to copper will allow a more complete picture to be developed. The amino acid arginine (Arg), which contains a guanidine functionality, has been shown to interact with copper ions via both the amine nitrogen and oxygen atom of the carboxylate group, in addition to forming both intra- and intermolecular hydrogen bonds.[2] These secondary H-bonding interactions have proved to be important in the self-organization of supramolecular assemblies, where, for example, the chirality of the arginine determines the "handedness" of the helicity in double helical structures formed by $[Cu(Arg)_2]^{2+}$ systems.[3]

We have recently exploited the neutral, bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) as a ligand in copper(I) cyano[4] and halide[5,6] complexes. The molecular structures of $CuCl(hppH)_2$ (**I**) and $CuCl(hppH)(PPh_3)$ (**II**) revealed monomeric, three-coordinate metals with intramolecular N*H*···Cl hydrogen bonds. The guanidine ligands in **I** and **II** were shown, by variable-temperature NMR spectroscopy, to be fluxional in solution, with $\Delta G^{\ddagger}$ values lower than in Cu(I) bipy and pyridine imine complexes,[7] rationalized by the formation of stable, five-membered metallacycles with these chelating ligands. To establish the importance of such secondary interactions in Cu(I) compounds with "hpp"-based ligands, we have designed two systems which remove the N*H* functionality (thus negating the opportunity of N*H*···X interactions) while retaining the N_{imine} group.

First, carbon[8] and silicon[9] linked poly(guanidyl) ligands have been developed, where additional stability is predicted as a consequence of the chelate effect. We have shown accordingly that bis(guanidyl)methane and -silane compounds, $H_2C\{hpp\}_2$ and $Me_2Si\{hpp\}_2$, chelate to copper(I) halides affording monomeric, three-coordinate complexes. Alternatively, the coordination chemistry of N-substituted guanidines, hppX ($X = SiMe_3$, Me), has been examined, where more complicated situations have been observed,

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(1) Stack, T. D. P. *Dalton Trans.* **2003**, 1881. Richards, R. L.; Durrant, M. C. *J. Chem. Res., Synop.* **2002**, 95.

(2) Ohata, N.; Masuda, H.; Yamauchi, O. *Inorg. Chim. Acta* **2000**, *300*, 749; de Farias, R. F.; Martínez, L.; Airoldi, C. *Transition Met. Chem.* **2002**, *27*, 253.

(3) Ohata, N.; Masuda, H.; Yamauchi, O. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 531.

(4) Coles, M. P.; Hitchcock, P. B. *Polyhedron* **2001**, *20*, 3027.

(5) Oakley, S. H.; Coles, M. P.; Hitchcock, P. B. *Inorg. Chem.* **2003**, *42*, 3154.

(6) Oakley, S. H.; Soria, D. B.; Coles, M. P.; Hitchcock, P. B. *Dalton Trans.* **2004**, 537.

(7) Desvergnes-Breuil, V.; Hebbe, V.; Dietrich-Buchecker, C.; Sauvage, J.-P.; Lacour, J. *Inorg. Chem.* **2003**, *42*, 255.

(8) Oakley, S. H.; Coles, M. P.; Hitchcock, P. B. *Inorg. Chem.* **2004**, submitted for publication.

(9) Oakley, S. H.; Coles, M. P.; Hitchcock, P. B. *Dalton Trans.* **2004**, 1113.

10.1021/ic0495970 CCC: $27.50

Table 1. Crystal Structure and Refinement Data for **1**−**3**

	1	**2**	**3**
formula	$C_{16}H_{30}Cl_2Cu_2N_6$	$C_{16}H_{30}Cu_2I_2N_6$	$C_{10}H_{21}ClCuN_3Si$
fw	504.44	687.34	310.38
temp (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst system	orthorhombic	orthorhombic	triclinic
space group	*Aba*2 (No. 41)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
a (Å)	16.8277(4)	9.5104(2)	7.8072(3)
b (Å)	12.2576(3)	15.1205(3)	9.6668(3)
c (Å)	9.7062(2)	15.3723(3)	10.7091(5)
α (deg)	90	90	111.982(3)
β (deg)	90	90	97.576(3)
γ (deg)	90	90	106.227(2)
V (Å^3)	2002.07(8)	2210.57(8)	693.77(5)
Z	4	4	2
D_{calc} (Mg/m^3)	1.67	2.07	1.49
abs coeff (mm^{-1})	2.41	4.73	1.83
θ range for data collcn (deg)	4.11−27.89	3.78−25.04	3.84−25.02
reflcns collcd	9022	21 411	5274
indepndnt reflcns	2064 (R_{int} = 0.042)	1943 (R_{int} = 0.052)	2349 (R_{int} = 0.043)
reflcns with $I > 2\sigma(I)$	1943	1708	2071
data/restraints/params	2064/1/180	1943/1/145	2349/0/229
goodness-of-fit on F^2	0.955	1.084	1.039
final R indices [$I > 2\sigma(I)$]	R1 = 0.024, wR2 = 0.054	R1 = 0.037, wR2 = 0.096	R1 = 0.032, wR2 = 0.064
R indices (all data)	R1 = 0.027, wR2 = 0.056	R1 = 0.045, wR2 = 0.101	R1 = 0.039, wR2 = 0.067
largest diff peak and hole (e Å^{-3})	0.362 and −0.419	1.12 and −1.34	0.30 and −0.29

dependent on both the nature of the nitrogen substituent and the copper(I) halide that is employed as the starting reagent.

Experimental Section

General Experimental Procedures. All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox operating at <1 ppm O_2. Solvents were dried over appropriate drying agents and degassed prior to use. The compounds CuCl, CuI, hppMe (Aldrich), ^nBuLi (2.5 M solution in hexanes, Acros), and hppH (Fluka) were purchased from commercial sources and used as received. $SiMe_3Cl$ (Aldrich) was distilled and stored under an atmosphere of nitrogen. The compound $hppSiMe_3$ was made according to literature procedures[10] and used without further purification. Elemental analyses were performed by S. Boyer at London Metropolitan University. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300.13 (^1H) and 75.76 ($^{13}C\{^1H\}$) MHz and a Bruker AMX 500 MHz at 500.13 (^1H) and 125.76 ($^{13}C\{^1H\}$). Proton and carbon chemical shifts were referenced internally to residual solvent resonances; coupling constants (*J*) are quoted in Hz.

Synthesis of [Cu(hppMe)$_2$][CuCl$_2$] (1). A solution of hppMe (0.5 mL, 3.48 mmol) in THF (10 mL) was degassed for 5 min by a subsurface sparge of N_2 and added dropwise to a slurry of CuCl (0.172 g, 1.74 mmol) in THF (25 mL). The CuCl partially dissolved during addition. The mixture was stirred at room temperature for 24 h, before being filtered from a small amount of particulate matter, to afford a clear, colorless solution. Removal of the solvent and crystallization from MeCN at −30 °C afforded pure **1** after several weeks. Yield: 0.10 g, 22% based on copper. Anal. Calcd for $C_{16}H_{30}N_6Cl_2Cu_2$: C, 38.10; H, 5.99; N, 16.66. Found: C, 38.25; H, 6.08; N, 16.73. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 3.17 (t, $^3J_{HH}$ = 5.5, 2H, CH_2), 3.03 (s, 3H, CH_3), 2.41 (m, 4H, CH_2), 2.29 (t, $^3J_{HH}$ = 6.0, 2H, CH_2), 1.31 (m, 2H, CH_2), 1.12 (m, 2H, CH_2). ^{13}C NMR (C_6D_6, 75 MHz, 298 K): δ 155.5 (CN_3), 48.1 (CH_2), 48.0 (CH_2), 47.8 (CH_2), 46.3 (CH_2), 38.6 (CH_3), 23.1 (CH_2), 22.2 (CH_2). MS (EI$^+$, *m/z*): 368 [Cu(hppMe)$_2$]$^+$.

Synthesis of [CuI(hppMe)]$_2$ (2). Compound **2** was made according to the procedure outlined for **1**, using hppMe (0.5 mL, 3.48 mmol) and CuI (0.331 g, 1.74 mmol). The pure compound was isolated as pale brown needles by crystallization from toluene. Yield: 0.25 g, 42% based on copper.

Anal. Calcd for $C_{16}H_{30}N_6Cu_2I_2$: C, 27.87; H, 4.39; N, 12.19. Found: C, 27.67; H, 4.23; N, 12.04. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 3.49 (m, 2H, CH_2), 3.07 (s, 3H, CH_3), 2.58 (t, $^3J_{HH}$ = 6.2, 4H, CH_2), 2.42 (t, $^3J_{HH}$ = 6.2, 2H, CH_2), 1.55 (m, 2H, CH_2), 1.31 (m, 2H, CH_2). ^{13}C NMR (C_6D_6, 75 MHz, 298 K): δ 153.5 (CN_3), 48.4 (CH_2), 48.2 (CH_2), 48.2 (CH_2), 45.3 (CH_2), 38.1 (CH_3), 23.6 (CH_2), 22.8 (CH_2).

Synthesis of CuCl(hppSiMe$_3$) (3). A solution of $hppSiMe_3$ (0.79 g, 3.72 mmol) in THF (20 mL) was added dropwise to a slurry of CuCl (0.178 g, 1.86 mmol) in THF (20 mL) and stirred at ambient temperature for 24 h. The resultant pale green solution was filtered and the extract concentrated and cooled at −30 °C, to afford colorless crystals of **3**. Yield: 0.38 g, 66%. Anal. Calcd for $C_{10}H_{21}N_3ClCuSi$: C, 38.70; H, 6.82; N, 13.54. Found: C, 38.34; H, 6.28; N, 12.24. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 2.83 (br, s, 4H, CH_2), 2.43 (m, 4H, CH_2), 1.29 (m, 4H, CH_2), 0.43 (s, 9H, CH_3). ^1H NMR (CD_2Cl_2, 500 MHz, 203 K): δ 3.24 (br s, 2H, CH_2), 3.18 (br s, 4H, CH_2), 2.97 (br s, 2H, CH_2), 1.77 (s, 4H, CH_2), 0.27 (s, 9H, CH_3). ^{13}C NMR (C_6D_6, 75 MHz, 298 K): δ *, 47.7 (CH_2), 43.3 (CH_2), 23.7(CH_2), 2.0 (CH_3) [* = CN_3 not observed]. ^{13}C NMR (CD_2Cl_2, 125 MHz, 298 K): δ 157.8 (CN_3), 48.3 (CH_2), 43.4 (br, CH_2), 24.1 (CH_2), 1.7 (CH_3). ^{13}C NMR (CD_2Cl_2, 125 MHz, 243 K, methylene resonances): δ 48.4 (CH_2), 48.3 (CH_2), 45.6 (br, CH_2), 41.2 (CH_2), 24.8 (CH_2), 23.1 (CH_2).

Crystallography. Details of the crystal data, intensity collection, and refinement for complexes **1**−**3** are listed in Table 1. Crystals were covered in an inert oil, and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[11] Additional features associated with each structure are described below:

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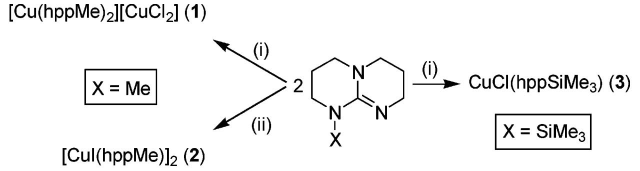
(10) Kummer, D.; Halim, S. H. A.; Kuhs, W.; Mattern, G. *J. Organomet. Chem.* **1993**, *446*, 51.

Scheme 1 [a]



[a] Key: (i) CuCl, THF; (ii) CuI, THF.

[Cu(hppMe)$_2$][CuCl$_2$] (1). The molecule lies on a crystallographic 2-fold axis.

[CuI(hppMe)]$_2$ (2). The hppMe ligand is disordered unequally over two overlapping orientations, and the higher occupancy orientation has a further disorder of the C(3) atom. *Because of the disorder, the ligand dimensions are unreliable.* The molecule lies on a crystallographic inversion center.

Results and Discussion

In contrast to the nonsubstituted parent guanidine compound hppH, NMR data of the *N*-methyl analogue (hppMe) are consistent with a static structure containing isolated C−N single and C═N double bonds with the result that each of the six methylene units of the ligand framework is therefore distinguishable in both ^{1}H and ^{13}C spectra. The coordination behavior of hppMe at copper(I) chloride was investigated (Scheme 1), with the resultant metal complex **1** displaying NMR properties similar to those of the noncoordinated ligand, consistent with the presence of localized C−N single and C═N double bonds. Combustion analysis of **1** indicated a ligand:metal:chloride ratio of 1:1:1; however, a peak was observed in the mass spectrum (EI$^+$, $m/z = 368$) corresponding to the bis(ligand)copper fragment, "Cu(hppMe)$_2$". The molecular structure of **1** was therefore investigated by X-ray diffraction, revealing that, in contrast to the simple coordination compounds formed for hppH and hppSiMe$_3$ (vide infra), complex **1** consists of the ion pair [Cu(hppMe)$_2$][CuCl$_2$]. The molecular structure is illustrated in Figures 1 and 2, crystal data are summarized in Table 1, and selected bond lengths and angles are in Table 2.

The cationic component of **1** consists of an approximately linear copper atom [N(1)−Cu(1)−N(1′) = 176.20(14)°] with two symmetry-related, N$_{\text{imine}}$-bound hppMe ligands. The Cu−N distance [1.894(2) Å] is relatively short in comparison with CuCl(hppH)$_2$ [1.962(2) and 1.966(2) Å], which likely reflects the attraction of the neutral ligand to the positive metal center. The coordination geometry at Cu(1) is completed by interaction with a [CuCl$_2$]$^-$ cuprate anion, with a short Cu···Cu distance of 2.7154(5) Å. There are no other inter- or intramolecular close contacts [e.g. Cl(1)−Cu(1) = 3.558 Å]. **1** is therefore a rare example of a compound containing an unsupported Cu(I)···Cu(I) interaction, with a significantly closer distance than found in the similarly charged 1,1′-bis(2-pyridyl)octamethylferrocenene (L) species, [CuL]$^+$[CuCl$_2$]$^-$ [Cu···Cu = 2.810(2) Å].[12] The anionic component of **1** also consists of an approximately linear copper [171.85(6)°] with Cu−Cl distances of 2.1140(8) Å. The cation "N−Cu−N" and anion "Cl−Cu−Cl" components are approximately perpendicular to each other, with torsion angles N(1)−Cu(1)−Cu(2)−Cl(1) 83.8° and N(1)−Cu(1)−Cu(2)−Cl(1′) −96.2° (Figure 2). Isotropic refinement of all of the hydrogen atoms indicated the closest intramolecular Cu···H$_{methyl}$ distance at Cu(1) to be 2.53 Å. While similar copper−hydrogen distances [2.49(4) Å] have been referred to as "semibridging interactions",[13] in view of the lack of further experimental evidence we are reluctant to refer to the coordination sphere at Cu(1) as containing agostic-type interactions. The π-bonding within the guanidine ligand may be considered as tending toward localized single [C(1)−N(2) = 1.362(3) Å] and double [C(1)−N(1) = 1.326(3) Å] carbon−nitrogen bonds, (Δ_{CN} value[14] of 0.036 Å) in agreement with the spectroscopic analysis.

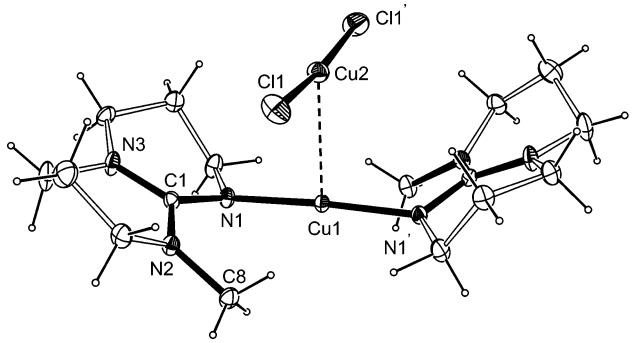


Figure 1. Molecular structure of [Cu(hppMe)$_2$][CuCl$_2$] (**1**), with thermal ellipsoids at the 30% probability level (prime, $-x$, $-y$, z).

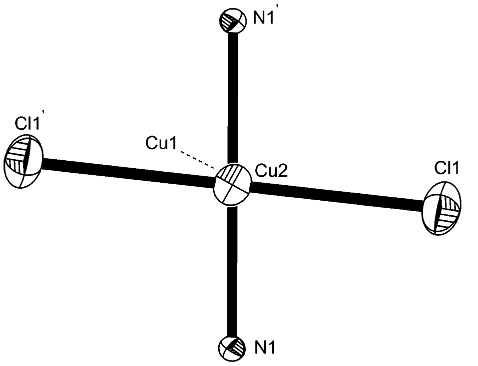


Figure 2. View of **1** down the Cu(2)···Cu(1) vector, showing the geometric arrangement of the two "CuX$_2$" fragments.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Cu(hppMe)$_2$][CuCl$_2$] (**1**)[a]

Cu(1)−Cu(2)	2.7154(5)	Cu(1)−N(1)	1.894(2)
Cu(2)−Cl(1)	2.1140(8)	C(1)−N(1)	1.327(3)
C(1)−N(2)	1.358(3)	C(1)−N(3)	1.345(3)
N(1)−Cu(1)−N(1′)	176.20(14)	Cl(1)−Cu(2)−Cl(1′)	171.85(6)
N(1)−Cu(1)−Cu(2)	91.90(7)	Cl(1)−Cu(2)−Cu(1)	94.07(3)

[a] Symmetry transformations used to generate equivalent atoms: prime, $-x$, $-y$, z.

There have been several reports presented in the literature regarding the nature of closed-shell interactions between d^{10}

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(11) Sheldrick, G. M. In *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(12) Siemeling, U.; Vorfeld, U.; Neumann, B.; Stammler, H.-G. *Chem. Commun.* **1997**, 1723.

(13) Kiani, S.; Long, J. R.; Stavropoulos, P. *Inorg. Chim. Acta* **1997**, *263*, 357.

(14) Häfelinger, G.; Kuske, K. H. In *The Chemistry of the Amidines and Imidates*; Wiley: Chichester, U.K., 1991; Chapter 1, Vol. 2.

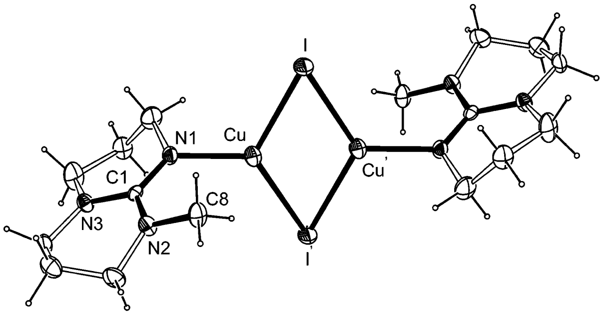

Figure 3. Molecular structure of [CuI(hppMe)$_2$]$_2$ (**2**), with thermal ellipsoids at the 30% probability level (prime, $-x$, $-y + 1$, $-z + 1$).

copper(I) centers.[15] Arguments have been presented for a "cuprophilic" attraction between the metals,[12] analogous to established "aurophilic" interactions (which have also been observed using neutral guanidine ligands[16]), and a recently reported close contact [2.9217(17) Å] between two similarly charged [CuCl$_2$]$^-$ ions strongly supports this theory.[17] However, in ion-pair complexes such as **1**, calculations have indicated that any interaction between such ions is likely to arise primarily from Coulombic attractions between the differently charged species.[18] Nevertheless, compound **1** represents the first example of a complex containing an unsupported Cu···Cu interaction incorporating guanidine ligands.

To further explore the possible formation of ion-pairs within this system, we investigated the analogous reaction between CuI and hppMe, where we reasoned the weaker copper–halogen bond was more likely to afford ionized products. We have previously noted that this reduction in bond strength manifests itself in the product CuI(hppH)$_2$, where a partially ionized structure exists in the solid state where five of the eight molecules in the unit cell consist of the ion-pair [Cu(hppH)$_2$]$^+$[I]$^-$ and the remainder contain a copper–iodine bond.[6] The reaction between 2 equiv of hppMe and CuI afforded pale brown crystals on workup, analyzing for "CuI(hppMe)" (**2**). The structure was solved by X-ray diffraction; the molecular structure is illustrated in Figures 3 and 4, crystal data are summarized in Table 1, and selected bond lengths and angles are in Table 3.

Compound **2** exists as the μ,μ-diiodo-bridged dimer in the solid state (Figure 3), as observed in related copper(I) iodides with bulky N-based donors.[6,19,20] The coordination sphere of the metal is completed by an imine-bound hppMe ligand, giving overall distorted trigonal planar geometry. Unfortunately, the ligand is present in two overlapping orientations at the metal (Figure 4) resulting in disorder that prohibits discussion of the bond lengths. However, it is clear that ionization has not occurred and **2** is present as the molecular species.

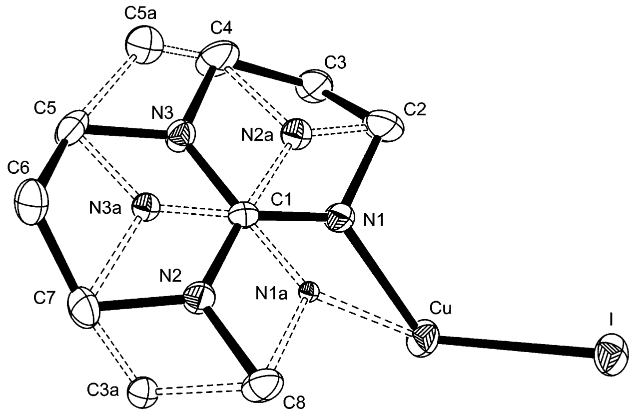

Figure 4. Asymmetric unit of **2** showing the disordered position of the ring. Major occupation is indicated by the solid bonds.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [CuI(hppMe)]$_2$ (**2**)[a]

Cu–N(1)	2.008(5)	Cu–I	2.5524(9)
Cu–I′	2.5578(9)		
N(1)–Cu–I	118.09(16)	N(1)–Cu–I′	121.87(16)
I–Cu–I′	119.35(3)	Cu–I–Cu′	60.65(3)

[a] Symmetry transformations used to generate equivalent atoms: prime, $-x$, $-y + 1$, $-z + 1$.

To further our understanding of how N-substitution influences the way in which guanidine ligands consisting of the hpp framework interact with copper(I) centers, the coordination of hppSiMe$_3$ was probed. Addition of hppSiMe$_3$ to a slurry of CuCl solubilized the metal salt, and colorless crystals of **3** formed upon cooling the solution to −30 °C (Scheme 1). The room-temperature ^{1}H and ^{13}C NMR spectra of **3** indicate a fluxional system in solution, with only three distinct resonances for the methylene groups rather than six predicted for localized C–N single and C=N double bonds. Cooling a CD$_2$Cl$_2$ solution to 203 K resulted in the resolution of only one of the methylene signals in contrast to CuCl(hppH)$_2$ in which all three signals were resolved at low temperature. Assuming a similar mechanism for the fluxional process, thermodynamic parameters calculated from these NMR measurements indicate a higher energy barrier for **3** ($\Delta G^{\ddagger} = 53.3$ kJ mol^{-1}) in comparison with CuCl(hppH)$_2$ (**I**) ($\Delta G^{\ddagger} = 45.8$ kJ mol^{-1}).[5] This is suggestive of either a stronger ligand–metal interaction (in agreement with the solid-state structure; vide infra) and/or a less labile N–Si bond in hppSiMe$_3$ compared with the corresponding N–H bond in hppH.

The molecular structure of **3** (Figure 5, Table 4) reveals that 1 equiv of the silylated ligand is accommodated at the metal center, binding as a neutral donor through the imine nitrogen atom. The resultant complex contains an approximately linear, two-coordinate copper center, with an N–Cu–Cl angle of 176.43(7)°. The closest intramolecular copper–hydrogen distance of 2.612 Å cannot be considered a bonding interaction, and in contrast to related compounds containing nitrogen donor groups where the metal is stabilized by intermolecular hydrogen bonding[20] or association with a

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(15) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(16) Schneider, W.; Bauer, A.; Schier, A.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 1417.

(17) Köhn, R. D.; Seifert, G.; Pan, Z.; Mahon, M. F.; Kociok-Köhn, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 793.

(18) Poblet, J.-M.; Bénard, M. *Chem. Commun.* **1998**, 1179.

(19) Healy, P. C.; Pakawatchai, C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1905. Campbell, J. A.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 1937.

(20) Healy, P. C.; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 137.

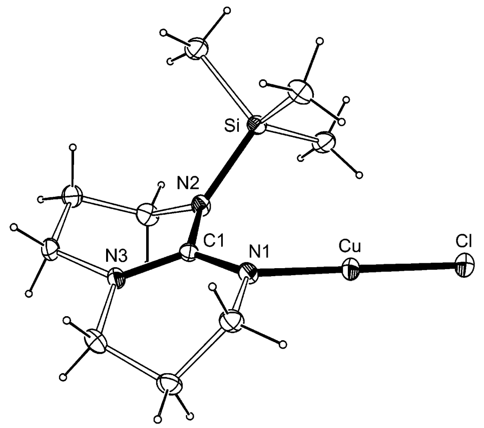


Figure 5. Molecular structure of CuCl(hppSiMe$_3$) (**3**), with thermal ellipsoids at the 30% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for CuCl(hppSiMe$_3$) (**3**)

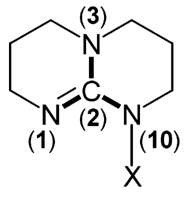
Cu−N(1)	1.877(2)	Cu−Cl	2.1022(7)
C(1)−N(1)	1.315(3)	C(1)−N(2)	1.376(3)
C(1)−N(3)	1.356(3)		
N(1)−Cu−Cl	176.43(7)	Cu−N(1)−C(1)	124.78(17)
Cu−N(1)−C(2)	116.80(17)	C(1)−N(1)−C(2)	117.0(2)
C(1)−N(2)−Si	127.87(16)	C(7)−N(2)−Si	116.17(8)
C(1)−N(2)−C(7)	113.9(2)	C(1)−N(3)−C(4)	122.3(2)
C(1)−N(3)−C(5)	124.8(2)	C(4)−N(3)−C(5)	112.9(2)

neighboring cuprous chloride group,[21] the next closest intermolecular copper−hydrogen distance is 3.260 Å. This is well above the range for such an interaction as indicated in the Cambridge Structural Database (1.406−2.202 Å),[22] and hence, we conclude **3** consists of a strictly two coordinate copper center. The copper−nitrogen distance in **3** [1.877(2) Å] is also shorter than in the bis-hppH complex, a likely consequence of reduced steric crowding at the metal center. The carbon−nitrogen distances within the hppSiMe$_3$ maybe considered predominantly localized, where a relatively large Δ_{CN} value of 0.06 Å, in comparison to **1**, is consistent with reduced delocalization of across the amidine unit.

Table 5. Natural Charges from Natural Population Analysis [Method MP2; Basis Set 6-31G(d)] for hppH, hppMe, and hppSiMe$_3$[a]

	hppH	hppMe	hppSiMe$_3$
N(1)	−0.682	−0.684	−0.721
C(2)	+0.758	+0.764	+0.788
N(10)	−0.743	−0.576	−0.993
N(3)	−0.598	−0.596	−0.594

[a] Refer to Figure 6 for the atomic numbering scheme.



X = H, Me, SiMe$_3$

Figure 6. Number scheme adopted for the natural population analysis of hppH, hppMe, and hppSiMe$_3$.

We reason that a major factor contributing to the formation of the structures reported in this contribution is the prohibition of stabilization via inter- or intramolecular N*H* hydrogen bonding. Natural population analysis [method MP2; basis set 6-31G(d)] performed on the compounds hppH, hppMe, and hppSiMe$_3$ indicate that the charge associated with the N$_{\text{imine}}$ atom is essentially identical for the hydrogen- and methyl-substituted compounds (Table 5, Figure 6) suggesting that the structural differences observed between CuCl(hppH)$_2$ and [Cu(hppMe)$_2$][CuCl$_2$] are mainly steric in origin. A slightly greater negative charge is associated with the corresponding nitrogen in the silyl-substituted guanidine, although discussion of these data in terms of a shorter copper−nitrogen bond distance in **3** is complicated by the low coordination number compared with the other copper guanidinate structures and the formal charge associated with compound **1**.

In summary we have shown that prohibiting hydrogen bonding through substitution at the N*H* position leads to formation of a number of different structural motifs including bimetallic copper species, [Cu(hppMe)$_2$][CuCl$_2$] (**1**), which contains an example of a short, unsupported Cu(I)···Cu(I) interaction, the corresponding dimer [CuI(hppMe)]$_2$ (**2**), formed with copper(I) iodide, and the simple two coordinate complex, CuCl(hppSiMe$_3$) (**3**). These data suggest the formation of intramolecular NH···X bonds play an important role in the stabilization of the three-coordinate molecular structures previously noted.

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Supporting Information Available: X-ray crystallographic files for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Thompson, J. S.; Whitney, J. F. *Acta Crystallogr., Sect. C* **1984**, *40*, 756.

(22) Careri, M.; Elviri, L.; Lanfranchi, M.; Marchiò, L.; Mora, C.; Pellinghelli, M. A. *Inorg. Chem.* **2003**, *42*, 2109.